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X-ray structural analysis of 1H, 4H-terahydroquinolizino-(9, 9a,1gh) coumarin

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Abstract The crystal structure of 1H,4H-terahydroquinolizino-(9, 9a, 1gh) coumarin ($C_{15}H_{15}NO_2$) has been determined by X-ray crystallographic techniques. The compound crystallizes in monoclinic space group $P2_1/n$ with a = 8.115(3), b = 19.067(10), c = 8.383(6) Å, β = 115.45(15)°, Z = 4. The structure has been solved by direct methods and refined to reliability index of 5.9%. The fused benzene and pyrone rings are planar. The piperidine ring C of the molecule adopts a *distorted sofa* conformation whereas the piperidine ring D exists in *distorted chair* conformation. The crystal structure is stabilized by intermolecular C-H . O hydrogen bonds.

Keywords : Coumarin derivative, structure analysis, hydrogen bonds

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Coumarins exhibit a wide spectrum of biological activity including antithrombotic and vasodilating effects on coronary vessels, a tonic influence on capillary blood vessels, reduction in blood pressure, antispastic and photosensitizing effects [1]. They are found as heterosides in many dicotyledonous families, *e.g. Apiaceae, Asteraceae, Fabiaceae, Moraceae, Rosaceae, Rubiaceae and Solanaceae* [2].

Coumarins derivatives are efficient laser dyes in the blue and green region of the spectrum [3]. The mobility of the amino group reduces the fluorescence efficiency of these dyes in polar solvents [3-5] but with a structurally rigid amino group, these derivatives show a high quantum yield of fluorescence in polar solvents [5, 6]. X-ray studies of the title compound 1H, 4H-tetrahydroquinizilino-(9, 9a, 1gh) coumarin (I), have been carried out to determine its three-dimensional structure and also to understand the role of hydrogen bonding in the molecular packing. The chemical structure of this compound is shown in Figure 1.

The title compoud was procured from Aldrich Chemical Company (U.S.A.) and its crystallization was tried with a variety of organic solvent systems. Good quality single crystals of (I) were grown using toluene as solvent. A white rectangular shaped single crystal of (I) with dimensions 0.3 × 0.2 × 0.2 mm was mounted on an Enraf-Nonius CAD-4 diffractometer for automatic intensity data collection using MoKα radiation (λ = 0.71069 Å). The compound crystallizes in monoclinic space group $P2_1/n$ with unit cell parameters a = 8.115(3), b = 19.067(10), c = 8.383(6) Å and β = 115.45(15)°. $\omega / 2\theta$ scan mode was employed for data collection with θ-range of 2.14 – 24.96°. A total of 2285 reflections were measured and out of which 2058 were found unique. Two standard reflections (3 2 1) and (1 0 3) measured after every 100 reflections and showed no significant variation in intensity. Reflection data were corrected for Lorentz and polarization effects and no absorption correction was applied.

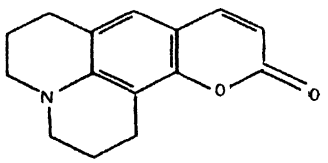

Figure 1. Chemical structure of 1H, 4H-tetrahydroquinizilino-(9, 9a, 1gh) coumarin.

The structure was determined by direct methods using SHELXS86 software [7]. Full matrix least-squares refinement of

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the non-hydrogen atoms including their thermal parameters was carried out using SHELXL93 software [8]. Final refinement with anisotropic thermal parameters of non-hydrogen atoms and fixing the hydrogen atoms stereochemically resulted into $R = 0.0598$, $wR2 = 0.1337$. Atomic scattering factors were taken from International Tables for Crystallography (Tables 4.2.6.8 and 6.1.1.4, Vol. C, 1992). The crystallographic data for compound (I) are summarized in Table 1.

Table 1. Crystal data and structure refinement details.

Crystal description	Rectangular plates
Empirical formula	$C_{14}H_{11}NO_2$
Formula weight	241.28
Temperature	293(2) K
Radiation	MoKα
Wavelength	0.71069 Å
Unit cell dimensions	a = 8.115(3), b = 19.067(10) c = 8.383 (6) Å, β = 115.45(15)°
Volume	1171.2(11) Å^3
Crystal system	Monoclinic
Space group	$P2_1/n$
Z, Calculated density	4, 1.368 Mg/m^3
F(000)	512
No. of reflections collected	2285
Reflections unique	2058
Reflections observed [$I > 2\sigma(I)$]	1090
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2058 / 0 /163
Goodness-of-fit on F^2	0.950
Final R indices [$F_o > 4\sigma F_o$]	R1 = 0.0598, wR2 = 0.1337
R indices (all data)	R1 = 0.1149, wR2 = 0.1548
Largest diff. peak and hole	0.26 < $\Delta\rho$ < − 0.31 e A^{-3}

The final atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are given in Table 2. The bond distances and bond angles are presented in Table 3. An ORTEP view of the molecule with the atomic numbering scheme is shown in Figure 2[9]. The geometrical calculations were performed by using the PARST program [10].

The bond distances and bond angles in the coumarin moeity are normal and are in good agreement with analogous structures [11-15]. The fused benzene ring A and pyrone ring B are almost planar and dihedral angle between the two rings is 0.6(1)°, thus making the coumarin moiety close to planar. The piperidine ring C of the molecule adopts *distorted sofa* conformation with asymmetry parameters [16] $\Delta Cs(C7) = 8.89$ and piperdine ring D of the molecule exists in *distorted chair* conformation with

Table 2. Atomic coordinates and equivalent isotropic thermal parameters (Å^2) for all the non-hydrogen atoms (e.s.d.'s in parentheses)

Atom			Z	U$_{eq}$*
O1	0.1633 (2)	0.4015(1)	0.3051 (2)	0.048 (1)
C2	0.1321 (4)	0.3366 (2)	0.2251 (4)	0.054 (1)
C3	−0.0376 (4)	0.3269 (2)	0.0719 (4)	0.055 (1)
C4	−0.1581 (4)	0.3794 (1)	0.0090 (3)	0.050 (1)
C5	−0.2453 (3)	0.5038 (1)	0.0378 (3)	0.043 (1)
C6	−0.2069 (3)	0.5666 (1)	0.1254 (3)	0.042 (1)
C7	−0.0360 (3)	0.5746 (1)	0.2789 (3)	0.038 (1)
C8	0.0869 (3)	0.5176 (1)	0.3368 (3)	0.039 (1)
C9	0.0394 (3)	0.4560 (1)	0.2428 (3)	0.040 (1)
C10	−0.1261 (3)	0.4462 (1)	0.0926 (3)	0.042 (1)
O11	0.2528 (3)	0.2934 (1)	0.2907 (3)	0.077 (1)
C12	−0.3369 (3)	0.6276 (1)	0.0693 (3)	0.054 (1)
C13	−0.3205 (4)	0.6680 (2)	0.2327 (4)	0.058 (1)
C14	−0.1265 (4)	0.6934 (2)	0.3298 (4)	0.062 (1)
N15	0.0055 (3)	0.6365 (1)	0.3697 (3)	0.049 (1)
C16	0.1860 (4)	0.6518 (2)	0.5071 (4)	0.063 (1)
C17	0.3289 (4)	0.6021 (2)	0.5125 (4)	0.064 (1)
C18	0.2667 (3)	0.5268 (1)	0.4975 (3)	0.052 (1)

$U^*_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a^*_i a^*_j (a_i . a_j)$

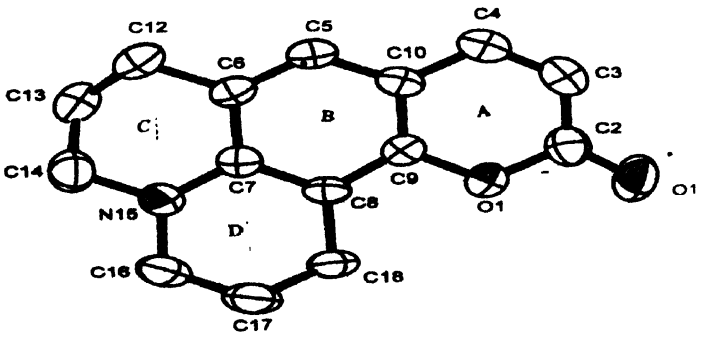

Figure 2. ORTEP view of the molecule, with displacement ellipsoids drawn at the 50% probability level.

asymmetry parameters $\Delta C_2(C7-C15) = 13.2$ and $\Delta Cs(C7) = 12.2$.

The molecules of (I) are linked by two intermolecular C-H...O hydrogen bonds as given in Table 4. The symmetry related O11 at (x-1/2, $-y$ + 1/2, +z−1/2) and (−x, −y+1), −z) are hydrogen bonded to C3 and C12 at (x, y, z). Based on the compiled data for a large number of C–H...O contacts, Steiner and Desiraju [17] find significant statistical directionality and the C-H...O interactions in (*I*) may be termed as 'weak' hydrogen bond, with a greater contribution to packing forces than simple van der Waals interactions. A view of the molecules down c-axis in the

Table 3. Bond distances (Å) and bond angles (°) for all non-hydrogen atoms (e.s.d.'s are given in parentheses).

O1 – C2	1.378 (4)	N15 – C14	1.459 (4)
O1 – C9	1.383 (3)	N15 – C16	1.452 (3)
C2 – O11	1.215 (4)	N15 – C7	1.366 (4)
C8 – C9	1.374 (3)	C14 – C13	1.508 (4)
C6 – C7	1.438 (3)	C17 – C16	1.483 (5)
C8 – C18	1.512 (3)	C18 – C17	1.509 (4)
C13 – C12	1.527 (4)	C12 – C6	1.503 (3)
C16 – N15 – C7	122.6 (2)	C18 – C8 – C7	119.0 (2)
C14 – N15 – C7	122.3 (2)	C8 – C18 – C17	110.2 (2)
C2 – O1 – C9	122.6 (2)	C18 – C17 – C16	112.1 (2)
N15 – C14 – C13	112.2 (2)	N15 – C16 – C17	113.9 (2)
C14 – C13 – C12	108.3 (2)	N15 – C7 – C8	120.3 (1)
C13 – C12 – C6	109.3 (2)	N15 – C7 – C6	120.1 (2)
C12 – C6 – C7	118.4 (2)		

Table 4. Geometry of intermolecular interaction (e.s.d's are given in parentheses)

D–H .A	D A (Å)	H A (Å)	D–H A (°)
C3–H3. O11$^{(i)}$	3.29 (4)	2.35 (4)	153.1 (1)
C12–H12B. .O11$^{(ii)}$	3.69 (4)	2.76 (4)	161.5 (4)

Symmetry code : (i) $x - 1/2, -y + 1/2, z - 1/2$; (ii) $-x, -y + 1, -z$.

unit cell shows their placement in reversed orientation (Figure 3).

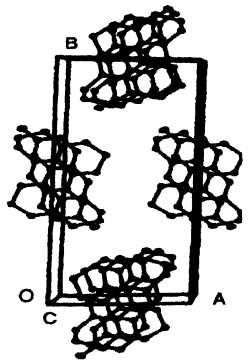

Figure 3. Packing diagram, viewed down the *c*-axis.

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